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Metal-Based Nanomaterials in Sustainable Pest Management: Assessing the Impact of Copper Nanoparticles on *Spodoptera frugiperda*

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Abstract

The fall armyworm (*Spodoptera frugiperda*) represents a significant threat to global food security, while traditional synthetic pesticides have led to considerable environmental consequences, including the loss of biodiversity and the emergence of widespread pest resistance. Copper nanoparticles (CuNPs) have surfaced as viable alternatives, providing potent insecticidal properties along with environmental compatibility. This review examines the function of CuNPs in sustainable pest management strategies against *S frugiperda*, delving into green synthesis techniques, the mechanisms of insecticidal action such as the induction of oxidative stress and neurotoxicity, and assessing efficacy data. Current research indicates that CuNPs can achieve mortality rates surpassing 90% in *S frugiperda* larvae, while exhibiting reduced environmental persistence in comparison to conventional pesticides. However, there remain knowledge gaps concerning multigenerational effects and the implications for non-target organisms, necessitating further research prior to widespread implementation.

Keywords: Copper nanoparticles, *Spodoptera frugiperda,* nanopesticides, green synthesis, oxidative stress, integrated pest management.

1. Introduction

The global agricultural sector is confronted with an increasing challenge: the need to boost crop yields to support a growing population while simultaneously reducing environmental harm. Insect pests are responsible for annual losses ranging from 20% to 40% of worldwide agricultural production [1]. The fall armyworm, *Spodoptera frugiperda*, which originated in the Americas, has rapidly disseminated to Africa, Asia, and Oceania, posing a threat to maize, rice, sorghum, and more than 350 plant species [2]. Its rapid reproduction and ability to develop resistance to various classes of insecticides render it one of the most pressing agricultural issues [3].

Conventional pest control methods have largely relied on synthetic chemical insecticides such as organophosphates, pyrethroids, and carbamates. Nevertheless, the environmental consequences, including non-target toxicity, groundwater contamination, and bioaccumulation, have become increasingly apparent [4]. Resistance among target populations has led to a cycle of rising application rates and reduced effectiveness, with documented resistance in *S frugiperda* to organophosphates, pyrethroids, and diamides [5].

Nanotechnology facilitates the creation of materials with customized physicochemical properties at the nanoscale of 1-100 nanometers. Metal-based nanomaterials exhibit unique characteristics, such as increased surface area-to-volume ratios and enhanced reactivity [6]. Copper nanoparticles (CuNPs) have attracted attention due to the antimicrobial properties of copper, its role as a micronutrient for plants, and its relatively low toxicity to mammals [7]. This review consolidates existing knowledge on the use of CuNPs for the management of *S frugiperda*, exploring synthesis methods, mechanisms of action, efficacy data, and environmental considerations.

2. Overview of Nanotechnology in Agricultural Pest Management

Nanotechnology refers to the manipulation of matter at scales where materials exhibit properties that differ from those of individual atoms and bulk materials [8]. In the field of agriculture, its applications encompass controlled-release formulations, targeted delivery systems, nanosensors, and nanopesticides that employ innovative modes of action. The nanoformulations of existing active ingredients can enhance efficacy by improving dispersion and penetration while simultaneously reducing application rates. Engineered nanomaterials can serve as active ingredients by leveraging intrinsic toxicity mechanisms that are distinct from those of conventional pesticides [9].

Metal-based nanomaterials are crucial due to their diverse mechanisms and relative ease of synthesis. Silver nanoparticles have been extensively studied for their antimicrobial properties, whereas zinc oxide and titanium dioxide nanoparticles produce reactive oxygen species through photocatalytic processes. Copper-based nanomaterials offer specific advantages, including lower costs compared to silver, a well-established regulatory history, and the dual functionality of acting as both a pesticide and a micronutrient fertilizer [10].

3. Copper Nanoparticles: Properties and Synthesis Approaches

Physicochemical Properties: The insecticidal efficacy of CuNPs is intrinsically associated with particle size, where smaller nanoparticles (10-50 nm) exhibit higher surface-to-volume ratios that enhance the release of copper ions and contact-mediated effects [11]. The surface charge plays a crucial role in colloidal stability and interactions with membranes, with positively charged nanoparticles demonstrating increased cellular uptake. The morphology, which includes spherical, rod-shaped, and plate-like structures, influences biological activity by affecting membrane penetration and reactivity.

Green Synthesis: The plant-mediated synthesis utilizes the reducing and stabilizing properties of phytochemicals such as flavonoids, phenolic acids, and terpenoids found in plant extracts [12]. *Azadirachta indica* (neem) produces CuNPs that exhibit significant insecticidal properties, which are attributed to the synergistic interaction between copper toxicity and azadirachtin derived from neem. Extracts from *Ocimum sanctum* (tulsi) yield CuNPs with potent larvicidal activity against *S frugiperda*, with the phenolic content playing a role in both stabilization and biological effectiveness [13]. Green synthesis provides environmental benefits and cost reductions; however, the challenges of variability between batches necessitate the establishment of standardized protocols.

4. Mechanisms of Action in Insect Pests

Oxidative Stress: Copper nanoparticles (CuNPs) trigger Fenton-type reactions that generate hydroxyl radicals, superoxide anions, and hydrogen peroxide [14]. These reactive species surpass the capacity of endogenous antioxidant defenses, leading to lipid peroxidation, protein carbonylation, and DNA damage. In *Spodoptera frugiperda*, exposure results in elevated malondialdehyde levels and modifies the activities of superoxide dismutase and catalase.

Membrane Disruption: CuNPs interact with negatively charged phospholipid headgroups, altering membrane fluidity and permeability. This disruption leads to uncontrolled ion fluxes and leakage of cellular contents. In midgut epithelial cells, damage to the membrane impairs nutrient absorption and the barrier function.

Neurotoxicity: The inhibition of acetylcholinesterase (AChE) is a notable neurotoxic mechanism. Exposure to CuNPs decreases AChE activity in the nervous tissues of insects, resulting in the accumulation of acetylcholine, prolonged postsynaptic excitation, and paralysis [15]. In *Spodoptera frugiperda*, concentration-dependent reductions in AChE activity are associated with behavioral abnormalities.

Detoxification Disruption: CuNPs affect cytochrome P450 monooxygenases, glutathione S-transferases, and carboxylesterases, hindering the insect's ability to metabolize toxins. This increases vulnerability to other control agents, presenting a potential for synergistic effects.

Genotoxic Effects: CuNPs infiltrate reproductive tissues, leading to DNA damage, decreased fecundity, and transgenerational impacts, including reduced egg production and hatching rates [16].

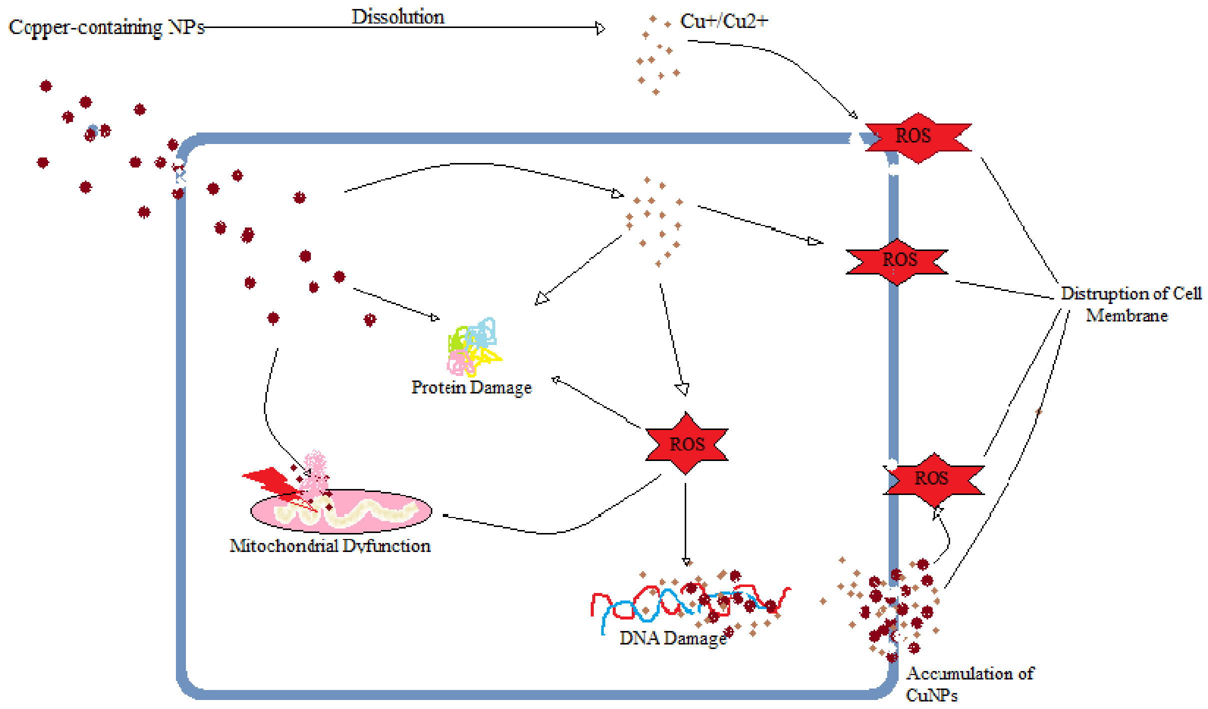

Fig.1: Mechanisms of Action in Insect gut cells

5. Effects on Spodoptera frugiperda

Larvicidal Activity: Mortality rates that depend on concentration follow standard dose-response relationships, with LC_{50} values between 10-100 mg/L. Third-instar larvae show a higher level of vulnerability compared to later instars. Green-synthesized CuNPs derived from Ocimum sanctum achieved a mortality rate of 96% within 72 hours, with LC_{50} values approximately 40% lower than those produced chemically [17].

Antifeedant Effects: CuNPs cause significant behavioral changes regarding feeding. Larvae that come into contact with CuNP-treated surfaces consume considerably less plant material, which can be attributed to sensory detection, toxic effects after ingestion, or neurological damage. At a concentration of 50 mg/L, reductions in consumption of 85-90% have been recorded.

Developmental Disruption: Sublethal exposure extends the duration of the larval stage, diminishes pupal weights, and leads to morphological defects such as incomplete molting and failure to emerge as adults. These consequences indicate a disruption in ecdysteroid and juvenile hormone signaling.

Immune Suppression: There is a notable decrease in total hemocyte counts, accompanied by diminished phagocytic activity, which heightens vulnerability to entomopathogens [18].

6. Laboratory and Field Evidence

Laboratory Studies: Standardized bioassays determine LC_{50} values ranging from 15 to 85 mg/L, influenced by particle characteristics and the larval stage. Time-course studies indicate that toxicity develops over a period of 24 to 96 hours, with sublethal effects observable at concentrations 5 to 10 times lower than LC_{50} values.
Field Trials: Foliar application at rates of 100 to 500 g/ha resulted in a 70 to 90% reduction in *S frugiperda* larval populations when compared to untreated controls, demonstrating efficacy that is either comparable to or exceeds that of chlorpyrifos and cypermethrin [19]. Increases in crop yield of 15 to 25% are attributed to diminished pest damage and potential benefits from micronutrients. Observations indicate minimal phytotoxicity and effects on pollinators.

Comparative Efficacy: CuNPs maintain effectiveness against populations known to be resistant to traditional insecticides, indicating that they may employ multi-modal mechanisms to bypass common resistance pathways.

Synergistic Combinations: When combined with Bacillus thuringiensis toxins, these formulations result in higher mortality rates than would be expected from additive effects alone, with the synergism attributed to CuNP-induced disruption of the midgut, which enhances toxin accessibility.

7. Environmental and Ecological Considerations

Fate in Agricultural Systems: When applied to leaves, nanoparticles attach to the surface where they can be consumed by pests. Rain can wash these nanoparticles into the soil, where they undergo processes of dissolution, aggregation, and transformation that influence their bioavailability [20]. The dissolution process releases Cu^{2+} ions, which may be absorbed by plants, adsorbed in the soil, or leached into groundwater.

Non-Target Soil Organisms: Soil microbial communities exhibit varying degrees of sensitivity, with a temporary decrease in bacterial diversity followed by recovery over time. Nitrogen cycling processes are especially vulnerable. Earthworms experience sublethal effects on their growth and reproduction at concentrations relevant to agricultural practices.

Beneficial Arthropods: Honey bees are less sensitive than target pests, with LC_{50} values that are 10-100 times higher. Predatory insects show varied sensitivity, with ladybird beetles experiencing reduced predation, while lacewing larvae seem to be relatively tolerant.

Environmental Profile Comparison: CuO nanoparticles achieve a 65-70% reduction in renewable energy consumption and ecosystem quality degradation per unit of efficacy when compared to traditional copper fungicides, indicating improved efficacy and minimized off-target movement.

8. Integration into Sustainable Pest Management

IPM Compatibility: Copper nanoparticles (CuNPs) should be utilized as interventions when pest populations surpass economic thresholds, rather than as preventive treatments. Their rapid action and short environmental persistence facilitate application strategies based on these thresholds. Plants that express Bt toxins and are treated with CuNPs demonstrate either additive or synergistic effects in pest suppression.

Resistance Management: The presence of multi-modal mechanisms that include simultaneous oxidative, membrane, neurotoxic, and genotoxic effects creates significant obstacles to the evolution of resistance. Implementing a rotation strategy with biological insecticides, botanical insecticides, and conventional products that operate through different mechanisms can effectively delay the development of resistance.

Economic Considerations: The green synthesis of CuNPs using locally sourced plant materials can lead to a considerable decrease in production costs. Cost-effectiveness analyses reveal a 30-50% reduction in pest control expenses when compared to traditional programs, all while sustaining or enhancing yield.

9. Current Limitations and Future Prospects

Stability and Standardization: Nanoparticle suspensions can experience aggregation or chemical changes during storage. Drying to create wettable powders can prolong shelf life, but it may also modify the characteristics of rehydrated particles. The lack of standardized protocols for synthesis, characterization, and biological testing hinders the ability to compare results across different studies and affects regulatory approval processes.

Knowledge Gaps: The long-term effects of repeated applications, such as the accumulation of copper in soil and the impact on non-target population dynamics, are not sufficiently understood. There is a particular need for multigenerational studies involving non-target organisms. In most jurisdictions, regulatory approval pathways are still being developed, and the existing frameworks may not adequately address the properties of engineered nanomaterials.

Future Research Priorities: It is crucial to focus on elucidating molecular-level mechanisms, assessing transgenerational effects, optimizing green synthesis protocols, developing targeted delivery systems, and conducting multi-year field validations in various agroecological contexts.

Conclusion and Future Research

Copper nanoparticles signify a significant breakthrough in the sustainable management of *Spodoptera frugiperda*, showcasing potent insecticidal effects through mechanisms such as oxidative stress, membrane disruption, neurotoxicity, and reproductive impairment. The utilization of green synthesis methods facilitates environmentally friendly production, which may also enhance biological efficacy. Research indicates that their effectiveness is comparable to or exceeds that of traditional insecticides, even at reduced application rates, while also presenting favorable environmental attributes. Nonetheless, challenges related to nanoparticle stability, formulation standardization, long-term ecological effects, and regulatory frameworks necessitate further investigation prior to widespread implementation. With ongoing research funding and suitable regulatory supervision, copper nanoparticles have the potential to play a vital role in diversified pest management, thereby decreasing reliance on conventional synthetic insecticides and maintaining agricultural productivity.

Conflicts of interest: The authors stated that no conflicts of interest.

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